PATENT SPECIFICATION (11) 1 211 405

NO DRAWINGS

1211405

(21) Application No. 14298/68 (22) Filed 25 March 1968
(31) Convention Application No. F 51952 IVc/39b
(32) Filed 25 March 1967 in
(33) Germany (DT)
(45) Complete Specification published 4 Nov. 1970
(51) International Classification C 08 g 22/44
(52) Index at acceptance
C3R 32B1 32B2 32C10 32C12 32C13P 32C13S 32C23 32C9 32C9S 32D2 32D6A 32D6C 32D6D 32E1 32E9Q 32F1 32G1 32H1 32H2 32H3 32H4 32H5A 32H5B 32H5C 32H5D 32H5F 32H6 32H8 32J1 32J2A 32J2Y 32J3 32J4 32L1B 32L4C
B5N 17X 17Y 22X 22Y 241 252Y 254Y 255Y 298Y 299Y 31Y 344 353 526 574 577 598 64X 682 685 686 690 69Y 713 71X 754 781
C3C 1E2

(72) Inventors GERHARD GRÖGLER, ERWIN WINDEMUTH and HANS HOLTSCHMIDT

(54) PROCESS FOR THE PRODUCTION OF POLYURETHANE OR POLYUREA FOAM PLASTICS

(71) We, FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany of 509 Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of foam plastics, particularly polyurethane or polyurea foam plastics.

Processes for the production of foam plastics based on compounds which contain reactive hydrogen atoms, polyisocyanates, water and/or other blowing agents by the one-stage or two stage process are already known. By using reaction accelerators, emulsifiers, stabilisers and substances which control the pore size, the foam-forming reactions can be adjusted to one another, so that it is possible to produce foam plastics with different properties by mechanical processes on a large industrial scale (see for example Kunststoff-Handbuch, Vol. VII, Polyurethanes, pages 25—28. 96—120, 440—458).

A new process for the production of foam plastics based on isocyanates which affords important advantages has now been found which is based on the use of hydroxyl and/or aminopolyethers which may contain tertiary nitrogen atoms or on the use of hydroxyl or amino polyethers without tertiary nitrogen atoms and the most important feature of which is that acyclic or cyclic esters of acids of hexavalent sulphur are added to the foam forming components. These acyclic or cyclic esters of acids of hexavalent sulphur do not contain any reactive hydrogen atoms.

Accordingly the invention provides a process for the production of polyurethane or polyurea foam plastics in which polyethers which contain hydroxyl and/or primary or secondary amino groups, polyisocyanates, water and/or other blowing agents and foaming catalysts, are foamed with open chain or cyclic esters of acids of hexavalent sulphur, which esters do not contain any reactive hydrogen atoms.

The polyethers may, if desired, contain tertiary amino groups.

The process according to the invention has numerous advantages over those previously known. As is well known, foam plastics based on polyurethanes are combustible (see Kunstatsoff-Handbuch (Publishers Carl Hanser, Munich, (1966) Volume VII, Polyurethanes, page 475).

Many different measures have been proposed to combat this undesirable characteristic, e.g. the use of flame protective agents in relatively high doses, e.g. tris - (2 - chloroethyl) - phosphate or tris - (2,3 - dichloropropyl) - phosphate, mixtures of ammonium phosphate and metal oxides, or antimony oxide with aluminium or bismuth powder, which render the foam plastic difficultly inflammable or self-extinguishing on removal of the flame. These additives, however, impair the properties of the foam plastics and, in addition, have the disadvantage that their effect diminishes after prolonged storage. Moreover, their use

[Price

may often lead to difficulties in the mechanical production of foam plastics in that the insoluble inorganic flame protective agents sediment in the foam forming components and cause trouble in the complicated mechanical feed devices which are normally used. The foam plastics according to the invention, however, are distinguished by being difficulty inflammable without having the disadvantages which are caused by the addition of flame protective agents. With choice of suitable components, it is possible by means of the invention to obtain incombustible foam plastics.

If foam plastics of very low specific gravities are produced, which can easily be done, for example, by using large quantities of water, with correspondingly large quantities of diisocyanates, self ignition of the foam plastics is sometimes observed due to careless operating techniques. This generally does not occur in the production of foam plastics by the process according to the invention.

The process according to the invention thus differs very advantageously in many ways from the processes previously known for the production of foam plastics based on isocyanates.

If polyethers containing one or more tertiary nitrogen atoms are used, which are strongly basic, the foamable systems are distinguished not only by the advantages already mentioned but also by short setting times combined with rapid surface drying of the foam plastics.

Furthermore, those foam plasitcs which are based on polyols or polyether polyols containing tertiary nitrogen atoms are completely odourless.

The foam plastics produced according to the invention are further distinguished by improved adhesion to sheet structures in flame spraying. Another advantage is that when they are subjected to high frequency welding with thermoplastics, especially if the thermoplasts are in the form of foils, e.g. polyvinyl chloride foils, shorter welding times are required and at the same time firmer adhesion is obtained than with the conventional foam plastics based on polyethers.

The foam plastics produced according to the invention can be synthesised from hydroxyl polyethers or from polyethers that contain terminal primary or secondary amino groups. Suitable hydroxyl polyethers are linear or branched polyalkylene ether polyols which can be obtained e.g. by polyaddition reactions in which 1,2-alkylene oxides such as ethylene oxide, propylene oxide, 1,2- and 2,3-butylene oxide, epichlorohydrin, styrene oxide or cyclohexene oxide, either alone or in admixture with each other, are added to themselves or to low molecular weight initiator molecules such as water, glycols such as hexanediol-(1,6) and 1,3-butylene glycol, polyols such as trimethylolpropane, glycerol, pentaerythritol resorcinol, hydroquinone and sorbitol and mono- and/or oligosaccharides such as cane sugar, glucose, lactose or degraded starches. Other hydroxyl polyethers which may also be used, at least to a certain extent, are polytetrahydrofuran polyethers. Linear or branched polypropylene glycol ethers which contain predominantly 1,2-propylene oxide are especially suitable according to the invention. In the production of hydroxyl polyethers in which ethylene oxide is used, the latter may be added to the reaction at any stage of the polyaddition. Suitable aminopolyethers include for example, those given in U.S. Patent Specification 2,888,439.

Tertiary nitrogen-containing linear or branched polyalkylene ether polyols which may preferably be used according to the invention, which can be obtained from the 1,2-alkylene oxides mentioned above as examples in the same way as neutral polyalkylene ether polyols by polyaddition reactions with amines or amino alcohols are very suitable reactants for the invention either alone or mixed with non-basic polyalkylene either polyols. Suitable starting components for the production of these basic polyalkylene ether polyols are especially mono or polyamines which contain aliphatic primary and/or secondary amino groups. Examples which may be given are ammonia; alkylamines such as methylamine or ethylamine; diamines of the general formula $H_2N—(CH_2)_2—NH_2$ in which n is an integer from 2 to 12, such as ethylene diamine, tetramethylenediamine or hexamethylene diamine; polyamines of the general formula

$$H_2N\text{-}[CH_2—CH_2—NH]_n—CH_2—CH_2—NH_2$$

in which n is an integer from 1 to 6, such as diethylene triamine or triethylenetetramine; polyamines of the general formula

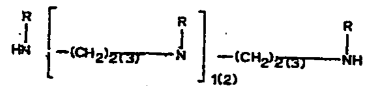
$$H_2N[—(CH_2)_3—NH]_n—(CH_2)_3—NH_2$$

in which n denotes 1 or 2, piperazine; β-aminoethyl piperazine; N,N' - bis - (β-aminoethyl) - piperazine; secondary amines of the general formula

$$\underset{\displaystyle R}{\overset{|}{HN}}—(CH_2—)_n—\underset{\displaystyle R}{\overset{|}{NH}}$$

in which n represents an integer from 2 to

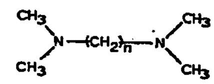
12 and R an alkyl radical, e.g. with 1 to 6 carbon atoms, preferably a methyl radical, such as N,N′-dimethylethylenediamine or N,N-dimethylhexamethylene diamines; and polyamines of the general formula.



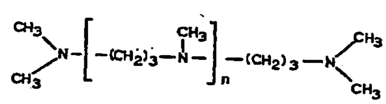
in which R denotes an alkyl group, e.g. with 1 to 6 carbon atoms, especially a methyl group. Other examples of suitable starting materials are ether amines obtained by the addition of acrylonitrile to mono- or polyfunctional alcohols, phenols or water followed by hydrogenation, e.g. 3-ethoxypropylamine or 3,3′-diaminodipropylether; polyamines obtained by the addition of acrylonitrile to primary or secondary mono- or polyfunctional amines followed by hydrogenation, such as 1-amino - 3 - methylaminopropane, 1 - amino-3 - dimethylaminopropane or 3,3′ - diaminopropylmethylamine. Amino alcohols such as 1,3-propanolamine, 1 - aminobutanol - 3, N-methylethanolamine and aminoalcohols obtained by the addition of acrylonitrile followed by hydrogenation are also suitable for the production of basic polyalkylene ether polyols. Other suitable starting materials are hydrazine, alkyl-hydrazines, symmetrical and asymmetrical dialkylhydrazines, guanidine, alkyl-substituted guanidines and aromatic mono- or polyfunctional primary and/or secondary amines such as toluene-2,4- or-2,6-diamines. Also suitable as starting materials are polyethers which contain tertiary amino groups and terminal primary and/or secondary amino groups, e.g. those polyethers which can be obtained from the corresponding polyalkylene ether polyols which contain tertiary nitrogen atoms by reacting them with p-nitrophenylisocyanates and reducing the nitro group by the process according to U.S. Patent Specification No. 2,888,439.

The said polyalkyleneether polyols or aminopolyethers which may contain tertiary amine groups may also be used together with other polyhydroxyl compounds which contain reactive hydrogen, e.g. hydroxyl polyesters prepared by conventional processes, which may also contain tertiary nitrogen atoms; polyester amides; polythioethers; polyacetals and polycarbonates which may also contain urethane groups. For the purpose of the invention, suitable compounds with reactive hydrogen atoms also include higher molecular weight compounds which have amino, carboxyl or mercapto groups, e.g. carboxyl-containing polyesters, or amino- or mercapto-containing polyurethanes.

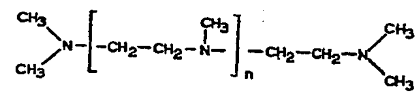
Suitable foaming catalysts are known in the art, for instance, tertiary amines and metal compounds. At least in the cases where no hydroxyl or aminopolyethers containing tertiary amino- groups are present tertiary amine catalysts are preferred. These include in particular strong basic aliphatic amines such as permethylated diamines of the general formula



in which n is an integer from 2 to 6; permethylated polyamines of the general formula



in which n is an integer from 1 to 4; permethylated polyamines of the general formula

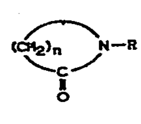


in which n denotes 1 or 2; tetramethyl - 1,3-butanediamine; N,N′-dialkylpiperazines such as N,N′-dimethylpiperazine; N - methyl - N′-dimethylaminoethylpiperazine; 1,4 - diaza-(2,2,2) - bicyclo - octane; N-alkylmorpholines such as N-methyl morpholines and amines which contain alkoxy groups, e.g. dimethyl-(3 - ethoxy propyl) - amine. Also to be mentioned are tertiary amines which contain reactive hydrogen atoms, which amines can be easily obtained by the addition of 1,2-alkylene oxides of the type given above to primary and/or secondary mono- or polyfunctional amines, e.g. dimethylaminoethanol; diethylamino - 2 - propanol; methyldiethanolamine; N,N′ - dimethyl - N,N′ - bis - (2 - hydroxyethyl) - ethylenediamine; N,N′ - dimethyl-N,N′ - bis - (2 - hydroxypropyl) - ethylenediamine; N,N - dimethyl - N′,N′ - bis - (2-hydroxypropyl) - ethylene - diamine; N,N,N′, N′ - tetra - (2 - hydroxypropyl)-hexamethylenediamine; N,N′,N″ - trimethyl - N,N′ - bis - (2 - hydroxypropyl)-diethylene triamine; N - (2 - hydroxypropyl)-morpholine; N - methyl - N - (2 - hydroxyethyl) - hexahydroaniline; and N,N′ - bis - (2-hydroxyethyl) - piperazine. Dimethylhydrazine or other alkyl-substituted hydrazines may also be used in accordance with the invention.

These diamines, which may be used either alone or in admixture with each other, are generally employed in quantities of 0.05 to 20, preferably 0.1 to 5 parts by weight to 100 parts by weight of hydroxyl or amino-polyethers.

Preferred metal catalysts are organic tin compounds and especially dibutyl tin dilaurate, lead octoate, lead naphthenate, tin - (II)-stearate, tin - (II) - oleate, ferric acetyl acetonate, bismuth nitrate, tin acetate, tin naphthenate, tin palmitate, tin stearate, dioctyl tin oxide, tin benzoate, tributyl tin laurate, ferric pentacarbonyl, ammonium molybdate, molybdic glycolate, vanadyl acetonate, copper acetyl acetonate, zinc stearate, tris - N-butyl arsine, tris - N - butyl oxide, dibutyl antimony laurate, manganous acetyl acetonate-dioctyl lead dichloride, and diisopropyl oxy-titanium - (IV) - acetyl acetonate.

Further foaming catalysts which could, if necessary, be used together with metal components, are: urea, N-alkyl ureas, N,N'-dialkyl urea or N,N'-diaryl ureas, e.g. N-methylurea, N,N'-dimethylurea, diethyl urea, dibutyl area or diphenyl urea, N,N,N',N'-tetraalkyl urea or tetraaryl urea, e.g. N,N,N'N' - tetramethyl urea as well as those ureas obtained by reaction of aliphatic, cycloaliphatic or aromatic primary or secondary amines with mono- or polyisocyanates. These ureas can be added as such or formed *in situ* in the foam formulation. Suitable amines are: ethylamine, butylamine, dibutylamine, tertiary butyl amine, cyclohexyl amine, aniline, N,N'-dimethyl ethylene diamine, N,N'-dimethyldiethylene triamine, pyrrolidine and piperidine. Furthermore, lactams or N-substituted lactams can be used as foaming catalysts, e.g. lactams of the following formula



R=a hydrogen atom or an alkyl or aryl group
n=3—12

These include pyrrolidone, N-methyl pyrrolidone, caprolactam, N-butyl caprolactam and N-methyl dodecane lactam. Acid amides, e.g. formamide, dimethyl formamide, acetamide, dimethyl propionamide or dimethyl butyramide, can also be used with success.

The above mentioned catalysts can also be added in admixture. Preferred amounts are 0,1 to 10 per cent by weight, preferably 0,5—5 per cent, based on the weight of polyether.

In order that the blowing reaction and polyurethane formation may proceed together, it is also frequently desirable to use mixtures of catalysts including mixtures of several types of catalyst. Foam stabilisers of the organo-siloxane-alkylene oxide block polymers type are advantageously used.

The following are given as polyisocyanates which may be used according to the invention: Aliphatic polyisocyanates such as 1,4-diisocyanatobutane; 1,6-diisocyanatohexane; m- and p-xylylenediisocyanate; dicyclohexylmethane - 4,4' - diisocyanate; cyclohexane-1,3- and cyclohexane - 1,4 - diisocyanate; 1-methylcyclohexane - 2,4- and -2,6 - diisocyanate; aromatic polyisocyanates such as 1-alkylbenzene - 2,4- and 2,6-diisocyanate, e.g. toluylene-2,4- and toluylene-2,6-diisocyanate as well as any isomeric mixtures of these two isocyanates; phenylene-1,3- and phenylene-1,4-diisocyanate; diphenylmethane - 4,4' - diisocyanate; naphthylene - 1,5 - diisocyanate; diphenylether - 4,4' - diisocyanate; 2,2' - dimethyldiphenylmethane - 4,4' - diisocyanate; polymethylenephenylpolyisocyanates obtained by aniline formaldehyde condensation followed by phosgenation; toleuene - 2,4,6 - triisocyanate; 4,4'4'' - triphenylmethane triisocyanate; 1 - methyl - 3,5,6 - trichlorobenzene - 2,4 - diisocyanate; and diisocyanato-mono-, di- and trichlorotoluenes obtained by side chain chlorination; the said polyisocyanates may be used either alone or in admixture with each other. Dimeric mono- and polyisocyanates may also be used, e.g. 3,3' - diisocyanato - 4,4' - dimethyl - diphenyluretdione. According to the invention, the polyisocyanates which can be prepared according to German Patent Specification No. 1,092,007 may also be used. Diisocyanates are preferably used.

It is a feature of the process according to the invention that acyclic or cyclic esters of acids of hexavalent sulphur are used, which acids contain no reactive hydrogen atoms, that is to say esters of acids of sulphur which no longer have Zerewitinoff-active hydrogen.

The following are examples of acyclic or cyclic esters of hexavalent sulphur which have no reactive hydrogen atoms: aliphatic alkyl sulphonates such as methyl, ethyl or n-butyl-methanesulphonate or methyl or ethyl ethane sulphonate; alkyl esters of vinyl-, propene-1- or propene-2-sulphonic acid, in which the alkyl radical may be linear or branched and may contain up to 6 carbon atoms; the ethyl ester of ethyl ether isothionic acid; the dimethyl, diethyl or di-n-propyl ester of sulphacetic acid, dimethyl or diethyl ester of 3-sulphopropionic acid; dimethyl ester of 2-sulpho-isobutyric acid; dimethylester of 4-sulphobutyric acid; alkyl esters of alkylthiosulphonic acid, such as methyl methanethiosulphonate or ethyl ethanethiosulphonate; aliphatic disulphonic acid esters such as the diethylester of 1,2-ethanedisulphonic acid or 1,3-propane disulphoniic acid; alkyl esters of benzyl sulphonic acid. Further, aromatic sul-

phonic acid alkyl esters in which the aromatic ring may be substituted and the alkyl group may be linear or branched, e.g. methyl, ethyl, propyl, butyl, or isobutyl esters of benzenesulphonic acid; the ethyl ester of p-chlorobenzenesulphonic acid; alkyl esters of o-, m- and p-toluenesulphonic acid, the alkyl radicals of which esters may be linear or branched and saturated or unsaturated and may contain hetero atoms, e.g. the methyl esters of o-, m- and p-toluenesulphonic acid; the isopropylester, n-butylester β-chloroethylester, n-dodecylester or oleyl ester of o-, m- or p-toluenesulphonic acid; alkylesters of naphthalene sulphonic acid and dialkylesters of sulphobenzoic acid, especially the dimethyl ester of sulphobenzoic acid; and alkyl esters of dialkyl-amidosulphonic acid, such as dimethylesters of diethyl or dibiutyl-amidosulphonic acid. Advantageously, the open chain or cyclic esters of acids containing hexavalent sulphur which have no reactive hydrogen atoms which are used are the monoesters.

Arylbissulphonic acid esters or arylpolysulphonic acid esters, such as the dimethylester of toluenebissulphonic acid may also be used, e.g. phenol disulphonic acid esters such as phenol - 2,6 - disulphonic acid ester, and also diphenylamine - 4,4′ - disulphonic acid ester. Metal alkylsulphates, dialkylsulphates such as dimethylsulphate, diethylsulphate, dibutylsulphate or glyoxal sulphate as well as cyclic esters of sulphuric acid, such as ethylene glycol sulphate may also be used. Sultones are also very suitable, especially γ-sultones such as γ-propanesultones, 1,8-naphthosultone, 2,3-benzopropanesultone and butanesultone as well as their alkyl substitution products such as 2 - methyl - pentanesultone - (2,4).

The esters of acids of hexavalent sulphur may be used alone or in admixture with each other. Additions of γ-alkanesultones such as γ-propanesultone and of C_1–C_3 alkylsubstituted benzene sulphonic acid methyl esters and mixtures thereof are especially advantageous.

According to the invention, the esters of acids of sulphur are preferably used in quantities of 1 to 15 parts by weight, more preferably 2 to 5 parts by weight for 100 parts by weight of polyalkylene ether polyol.

Various methods may be used for carrying out the process. Generally, in all the different methods used the retardation in the foaming process caused by the use of esters of acids of hexavalent sulphur is preferably compensated by a sufficiently large amount of tertiary amino groups so that the blowing reaction which liberates carbon dioxide, which reaction is based on the reaction between polyisocyanate and water, and the polymerising polyurethane formation brought about by the reaction between amino or hydroxypolyether and polyisocyanate are not impaired. The tertiary amino groups preferably being present in the starting material may be supplied to the system either by using tertiary amines such as those generally known as catalysts or those with reactive hydrogen atoms, or through the tertiary amino content of the basic hydroxyl or aminopolyethers which may be used.

One embodiment of the process according to the invention consists, for example, in reacting a hydroxyl or amino polyether which has no tertiary amino groups with a polyisocyanate, water, tertiary amines, other auxiliary substances and at least one ester of an acid of hexavalent sulphur which has no reactive hydrogen atoms, and at the same time effecting foaming. The quantity of polyisocyanate to be used depends on the reactive hydrogen atom content of the hydroxyl or aminopolyether and the quantity of water used, an overall balance of reactive H (including H_2O) to NCO— of 1 or more than 1 being generally employed. However, smaller quantities of polyisocyanate may be used in order to obtain special properties in the foam.

In another embodiment of the process according to the invention hydroxyl or aminopolyethers containing tertiary amino nitrogen, either alone or mixed with amino or hydroxyl polyethers which do not contain tertiary amino nitrogen, are foamed by the one stage process with polyisocyanates, water, auxiliary agents and an ester of an acid of hexavalent sulphur which does not contain reactive hydrogen atoms. Depending on the quantity and type of the basic hydroxyl polyether or aminopolyether containing nitrogen and of the ester of acids of sulphur which does not contain reactive hydrogen atoms, one may, when operating by this method, also include tertiary amines of the type already mentioned in order to control the foaming process in a desired direction as regards the expansion and setting times of the foamable mixture.

In one preferred embodiment of the process according to the invention a polyether which contains hydroxyl groups and/or amino groups and possibly also tertiary nitrogen is reacted in the single stage process with a solution in the polyisocyanate of open chain or cyclic esters of acids of hexavalent sulphur, which esters have no reactive hydrogen atoms, together with water and/or other blowing agents and, at least in the case where no polyethers containing tertiary amino nitrogen are present, with tertiary amines as catalysts and if desired other foaming catalysts.

In the embodiments of the process so far described, the esters of acids of hexavalent sulphur are added at the same time with the other components. According to a further embodiment, these are reacted with the reaction mixture or the components of the reaction mixture before the foaming process. Since the esters of acids of hexavalent sulphur are capable of quaternising nitrogen, in

this procedure lower and/or higher molecular weight basic hydroxyl polyethers are first completely or partially quaternised by reacting them with esters of acids of hexavalent sulphur at room temperature or at elevated temperatures. The quaternising reaction, which leads to an increase in viscosity of the reaction mixture depending upon the type of quaternising agent and the degree of quaternisation, is terminated when a constant viscosity is reached. Foam materials according to the process of the invention are obtained from these completely or partially quaternised basic polyalkylene ether polyols by the single stage process by mixing these with polyisocyanates, water, auxiliary agents and if desired tertiary amines.

These completely or partially quaternised basic polyols may, of course, also be foamed by the single stage process in admixture with neutral polyalkylene ether polyols or amino polyethers. In addition, the tertiary amines used as catalysts, which may still contain reactive hydrogen atoms, may, of course, be partly or completely quaternised with esters of acids of sulphur and added to the foamable systems to obtain foams according to the invention.

The so-called two-stage process, in which an isocyanate containing prepolymer is first prepared from a polyol by reaction with excess polyisocyanate and this prepolymer is then converted into a foam in a separate operation with water, catalysts and auxiliary agents, very often provides technical advantages with regard to working up, e.g. in the case of so-called mould foaming. This procedure may also be carried out in accordance with the invention. Thus prepolymers having free NCO groups are first prepared, if desired in a mixture with monomeric polyisocyanate, from hydroxyl polyethers that do not contain amino groups or from hydroxyl polyethers that contain tertiary amino groups or from hydroxyl polyethers that contain quaternised tertiary amino nitrogen or from mixtures of these components. Foams are obtained from these isocyanate-containing prepolymers by mixing these with water, tertiary amines, auxiliary agents and if desired also other polyisocyanates and an ester of an acid of hexavalent sulphur which ester does not contain reactive hydrogen atoms. Where a polyalkylene ether polyol which has previously been quaternised is used, the addition of an ester of an acid of hexavalent sulphur is generally no longer required although in some cases this possibility may be desirable. If a basic hydroxyl polyether is used or a basic polyalkylene ether polyol that has been only partially quaternised, the use of additional tertiary amine as catalysts may sometimes be omitted in the operation of foaming the resulting isocyanate-containing preadducts.

In the embodiments described, the carbon dioxide obtained from the reaction of isocyanate with water serves as the blowing agent for the formation of the foams. As in the known processes, the density of foam is regulated by the quantity of water used. Disubstituted ureas are formed in the reaction between isocyanate and water to serve as linking structural elements between the polyalkylene ether chains which have an elasticising action.

The addition of smaller quantities of water causes a reduction in the urea content in the foam with simultaneous increase in the density. In order to obtain foams with a low urea content and having a low density, additional blowing agents may be used such as low boiling liquids, especially fluorine- and chlorine-containing alkanes such as monofluorotrichloromethane, difluoro - dichloromethane or methylene chloride. According to the invention, these blowing agents may be used either in addition to water, or alone without any loss in the advantages obtained. By this means the physical properties of the foam can be still further varied in the desired manner.

The foams produced according to the invention are thus distinguished especially by being difficultly inflammable and, if suitable components are chosen, even incombustible. One may, of course, occasionally reinforce this effect by adding known flame protective agents such as tris - (2 - chloroethyl) - phosphate or tris - (2,3 - dichloropropyl) - phosphate, 2,3-dibromopropanol and others such as those described in Kunststoff-Handbuch (Carl Hanser Verlag, 1966), Volume VII, Polyurethanes, pages 110—111, but in many cases this is not necessary.

The known auxiliary agents may, of course, also be used for the production of the foam plastics according to the invention, e.g. organic metal catalysts, surface-active additives and foam stabilisers, cell regulators, plasticisers, substances that have a fungistatic and bacteriostatic action, dyes and pigments and inorganic fillers.

The invention is further illustrated by the following examples.

EXAMPLE 1

The following reaction mixtures (A and B) are added together:

A.	100 parts by weight of a		partly branched polypropylene glycol ether based on propylene oxide, trimethylolpropane and propanediol-(1,2) (OH number 56, molecular weight about 2500)
	0.25	”	1,4-diaza(2,2,2)-bicyclooctane
	0.3	”	tin(II)-ethyl hexoate
	1.2	”	of an organosiloxane-alkylene oxide block polymer
	3.0	”	water
B	41 parts by weight of		an isomeric mixture of 80% 2,4- and 20% 2,6-diisocyanatotoluene
	4.0		propane sultone

The mixture of the above components immediately starts to foam and after 100 seconds it forms an elastic foam the interior of which is set after 170 seconds and which has the following properties:

Weight per unit volume:	32 kg/m^3
Tensile strength:	1.3 $kg.wt./cm^2$
Elongation at break:	340%
Resistance to compression:	(40%) 33 p/m^3

According to the ASTM test D-1692, the foam obtained is self extinguishing and shows a combustible portion of 60 to 70 mm.

EXAMPLE 2

The following components A and B are mixed:

A	100 parts by weight of		a branched polypropylene glycol ether based on propylene oxide and and trimethylolpropane (OH number 56, molecular weight about 3000)
	0.3 parts by weight of		1,4-diaza(2,2,2)-bicyclooctane
	0.3	”	tin(II)-ethyl hexoate
	1.2	”	an organosiloxane-alkylene oxide block polymer
	3.0	”	water.
B	41 parts by weight of		an isomeric mixture of 80% 2,4- and 20% 2,6-diisocyanatotoluene
	4.0	”	of a mixture of 85% propane- and 15% butane sultone.

After a short expansion time (90 seconds) a self-extinguishing foam is obtained which has a combustible portion of 30 to 40 mm according to ASTN D—1692 and has the following mechanical properties:

Weight per unit volume:	31 kg/m^3
Tensile strength:	1.1 kg.wt/cm^2
Elongation at break:	250%
Resistance to compression:	(40%) 37 p/cm^3

EXAMPLE 3

The following mixtures A and B are combined:

A.	100	parts by weight of	a polypropylene glycol ether according to Example 1
	0.5	„	permethylated diethylene triamine
	0.35	„	tin(II)-ethylhexoate
	1.0	„	of an organosiloxane-alkyleneoxide block polymer
	3.0	„	water
B	40	parts by weight of	an isomeric mixture of 80% 2,4- and 20% 2,6-diisocyanatotoluene
	4.0	„	methyl p-toluenesulphonate.

The resulting elastic foam which is set internally after 85 seconds is difficulty inflammable; after removal of a flame directed towards the foam, extinction of the foam takes place immediately. The combustible portion is less than 20 mm according to ASTM D—1692.

The physical properties of the polyurethane foam are as follows:

Weight per unit volume:	34 kg/m^3
Tensile strength:	1.4 kg wt/cm^2
Elongation at break:	340%
Resistance to compression	(40%) 25 p/cm^3.

EXAMPLE 4

The following components are mixed:

A	100	parts by weight of	a partly branched polypropylene glycol ether which is modified with terminal ethylene oxide groups (OH number 46)
	0.5	„	N-methyl-N'-dimethylaminoethyl-piperazine
	0.4	„	tin(II)-ethyl hexoate
	1.0	„	of an organosiloxane-alkylene oxide block polymer
	3.0	„	water.
B	39	parts by weight of	an isomeric mixture of 80% 2,4- and 20% 2,6-diisocyanatotoluene
	3.0	„	methylbenzenesulphonate.

The resulting polyurethane foam is self extinguishing and has the following mechanical properties:

Weight per unit volume:	34 kg/m³
Tensile strength:	1.4 kg wt/cm²
Elongation at break:	305%
Resistance to compression:	(40%) 35 p/cm³

EXAMPLE 5

Component A having the following constitution:

A	100	parts by weight of	a polypropylene glycol ether according to Example 1
	2.0	,,	N,N′-dimethyl-N,N′-bis-(2-hydroxy-ethyl) ethylene diamine
	0.15	,,	permethylated diethylene triamine
	0.3	,,	tin(II)-ethyl hexoate
	1.0	,,	of an organosiloxane-alkylene oxide block polymer
	3.0	,,	water

is mixed with component B consisting of:—

43	parts by weight of	an isomeric mixture of 80% 2,4- and 20% 2,6-diisocyanatotoluene
4.5	,,	ethyl-p-toluenesulphonate.

The foam which forms after a short expansion time is elastic and has the following physical properties:

Weight per unit volume:	35 kp/m³
Tensile strength:	1.3 kg wt/cm²
Elongation at break:	320%
Resistance to compression:	(40%) 30 p/cm³

The foam is difficultly inflammable. The combustible portion only amounts to 20 to 25 mm.

EXAMPLE 6

100 parts by weight of a polyether-isocyanate prepolymer of NCO content 9.5% prepared from 100 parts by weight of the polypropylene glycol ether (OH number 56) indicated in Example 1 and 35 parts by weight of an isomeric mixture of 80 2,4- and 20% 2,6-diisocyanatotoluene are intimately mixed by stirring with 0.5 parts by weight of an organosiloxane-alkylene oxide block polymer and 4 parts by weight of a mixture of 85% propanesultone and 15% butanesultone. A mixture of 2 parts by weight of water, 0.5 parts by weight of oleic acid diethylamine and 4 parts by weight of N-methyl morpholine are then added. The reaction mixture immediately starts to foam, and after about 120 seconds yields a foam with slightly closed pores which according to ASTM D—1692 is incombustible.

EXAMPLE 7

100 Parts by weight of a polyether-isocyanate prepolymer that has an NCO content of 9.2% prepared from 98 parts by weight of the polypropylene glycol ether described in Example 1, 2 parts by weight of N,N′ - dimethyl - N,N′ - bis - (2 - hydroxypropyl) - ethylene diamine and 38 parts by weight of an isomeric mixture of 65% 2,4- and 35% 2,6-diisocyanatotoluene are stirred with 1.0 parts by weight of an organosiloxane-ethylene oxide block polymer and 3 parts by weight of ethyl benzene sulphonate. After a short interval, a mixture of 2.0 parts by weight of water, 0.5 parts by weight of oleic acid diethylamine and 0.75 parts by weight of permethylated diethylene triamine is added. The foam, which has slightly closed pores, has a high tensile strength and is self extinguishing.

EXAMPLE 8

The following reaction mixtures are combined:

A	100 parts by weight of		a branched aminopolyether based on propylene oxide and N,N′′-diisopropyl-diethylenetriamine; (OH number: 79)
	0.4	,,	tin(II)-ethylhexoate
	0.5	,,	of an organosiloxane-alkylene oxide block polymer
	3.0	,,	water.
B	41.5	,,	of an isomeric mixture of 80% 2,4- and 20% 2,6-diisocyanatotoluene
	5.0	,,	of a mixture of 70% propanesultone and 30% butanesultone.

The mixture immediately starts to foam, and after 50 seconds it forms an elastic foam which according to the ASTM test 1692 is self extinguishing and has a combustible portion of 25 to 30 mm.

EXAMPLE 9

The following mixtures A and B are added together:

A	100 parts by weight of		a branched polyether based on propylene oxide, ethylene oxide and trimethylolpropane (OH number 46)
	2.0	,,	N,N′-dimethyl-N,N′-bis-(2-hydroxypropyl)-ethylene diamine
	0.4	,,	tin(II)-ethylhexoate
	0.5	,,	of an organosiloxane-alkylene oxide block polymer
	3.0	,,	water
B	38.0 parts by weight		of an isomeric mixture of 80% 2,4- and 20% 2,6-diisocyanatotoluene
	3.1	,,	diethylsulphate.

After an expansion time of 75 seconds, a finely porous, elastic foam is obtained which according to the ASTM test 1692 is self-extinguishing, having a combustible portion of 40 to 45 mm.

EXAMPLE 10

A mixture of:

100 parts by weight of		a branched polyether based on propylene oxide, ethylene oxide and trimethylol propane (OH number 46)
2.0	„	N,N'-dimethyl-N,N'-bis-(2-hydroxypropyl)-ethylene diamine
0.5	„	tin(II)-ethylhexoate
0.5	„	of an organosiloxane-alkylene oxide block polymer
3.0	„	water
is combined with a mixture of		
38.0 parts by weight of		an isomeric mixture of 80% 2,4-and 20% 2,6-diisocyanatotoluene
2.2	„	methyl methanesulphonate.

An elastic, self-extinguishing foam is obtained which has a combustible portion of 35 to 40 mm.

EXAMPLE 11

Components A and B described below are mixed together:

A	60 parts by weight of		a partly branched polypropylene ether based on propanediol-(1,2) and trimethylolpropane; (OH number 56, molecular weight about 2500)
	40	„	of a slightly branched polyester based on adipic acid, diethylene glycol and trimethylolpropane (OH number 60)
	2.0	„	N,N'-dimethyl-N,N'-bis-(2-hydroxypropyl)-ethylenediamine
	0.3	„	tin(II)-ethyl hexoate
	0.5	„	of an organosiloxane-alkylene oxide block polymer
	3.0	„	water
B	38.0	„	of an isomeric mixture of 80% 2,4-and 20% 2,6-diisocyanatotoluene
	4.0	„	propanesultone.

The mixture of A and B immediately starts to foam, and a very soft, elastic foam is obtained which according to the ASTM test 1692 is self-extinguishing and has a combustible portion of 35 to 40 mm.

EXAMPLE 12

100 Parts by weight of a polyether-isocyanate prepolymer that has an NCO content of 9.5% and has been prepared from 100 parts by weight of a linear aminopolyether based on propylene oxide and methylamine (OH number 57) and 35.5 parts by weight of an isomeric mixture of 80% 2,4- and 20% 2,6-isocyanatotoluene are thoroughly stirred together with 0.5 parts by weight of a methyl polysiloxane and 3 parts by weight of propane sultone. A mixture of 2 parts by weight of water, 0.5 parts by weight of oleic acid diethylamine and 0.5 parts by weight of permethylated diethylene triamine is then added, when the mixture foams very quickly. An elastic foam is obtained which according to the ASTM test 1692 is incombustible.

EXAMPLE 13

100 Parts by weight of the polyether-isocyanate prepolymer according to Example 12 are stirred together with 0.5 parts by weight of an organosiloxane-alkylene oxide block polymer and 3. parts by weight of methyl

p-toluene-sulphonate, and a mixture of 2 parts by weight of water, 0.5 parts by weight of oleic acid diethylamine and 0.5 parts by weight of permethylated diethylene triamine is then added. A self extinguishing foam with slightly closed pores is obtained from the foamable mixture.

EXAMPLE 14

A mixture of 2 parts by weight of water, 2 parts by weight of N,N' - dimethyl - N,N'-bis - (2 - hydroxypropyl) - ethylene diamine, 0.5 parts by weight of permethylated diethylene triamine and 0.5 parts by weight of oleic acid diethylamine is added to 100 parts by weight of the polyether-isocyanate polymer of Example 12 which has been thoroughly mixed with 0.5 parts by weight of an organosiloxane-alkylene oxide block polymer and 3 parts by weight of propane sultone. After foaming of the mixture, a self-extinguishing elastic foam with slightly closed pores is obtained.

EXAMPLE 15

1 Parts by weight of an organosiloxane-alkylene oxide block polymer, 0.2 parts by weight of tin(II)-ethyl hexoate and 3.2 parts by weight of water are added to a mixture of 100 parts by weight of a partly branched polypropylene glycol ether polyol (OH number 56) and 2 parts by weight of N,N' - dimethyl - N,N' - bis - (2 - hydroxypropyl)-ethylene diamine, and this is then mixed with a solution of 3 parts by weight of methyl o-toluene sulphonate in 43 parts by weight of a mixture of toluene-2,4- and -2,6-diisocyanate in the isomeric ratio of 80:20. The mixture of components starts to foam; after an expansion time of 78 seconds, a finely porous, open cell, elastic foam has formed which according to the combustibility test ASTM 1962 is to be considered as self extinguishing, having a combustible portion of 42 mm.

An analogous result is obtained by using a mixture of equal parts of methyl-o- and p-toluene sulphonate dissolved in the said toluene diisocyanate mixture.

EXAMPLE 16

Employing the manual foaming process, 100 parts by weight of polyether B, described below, are reacted with

7.5	parts by weight	of allyl-p-toluenesulphonate
0.7	"	of an organosiloxane-alkylene oxide block polymer
0.6	"	tin(II)-ethyl hexoate
3.0	"	water
39.0	"	of a mixture of 2,4- and 2,6-toluylene diisocyanate in the ratio of 80:20,

the mixture expanding for about 45 seconds to form an elastic foam which is found in the combustion test ASTM D 1692 to be self-extinguishing after burning 30 to 40 mm.

EXAMPLE 17

In a manner analogous to Example 16, 100 parts by weight of B are reacted with

4.0	parts by weight	of allyl-p-toluenesulphonate
0.5	"	of an organosiloxane-alkylene oxide block polymer
0.5	"	of tin(II)-ethyl hexoate
3.0	"	water
39	"	of a mixture of 2,4- and 2,6-toluylene diisocyanate in the ratio of 80:20,

the mixture expanding for about 50 seconds and forming an elastic foam which in the combustion test according to ASTM D—1692 is self-extinguishing after burning 75 to 85 mm.

EXAMPLE 18

By stirring together a mixture of

160	parts	by weight of polyether A, described below
40	parts	by weight of component D, described below,
10	parts	by weight of allyl-p-toluenesulphonate,
2	parts	by weight of an organosiloxane-alkylene oxide block polymer,
0.8	parts	by weight of tin(II)-ethyl hexoate,
0.8	parts	by weight of diazabicyclo-octane,
6.4	parts	by weight of water and
82	parts	by weight of an isomeric mixture of 80% by weight of 2,4- and 20% by weight of 2,6-diisocyanatotoluene,

an elastic foam is obtained after an expansion time of 65 seconds, which foam is found in the combustion test according to ASTM D—1692 to be self-extinguishing after burning for 35 to 45 mm.

EXAMPLE 19

By reacting 100 parts by weight of B with 7.20 parts by weight of methyl p-toluene-sulphonate, about 50% of the tertiary amino groups contained in B are quaternised, the OH number at the same time falling from 51 to 50.

50	parts	by weight of this quaternised aminopolyether are reacted with
50	parts	by weight of A,
0.5	parts	by weight of an organosiloxane-alkylene oxide block polymer,
0.05	parts	by weight of tin(II)-ethyl hexoate,

0.5 parts by weight of a permethylated diethylene triamine,
3 parts by weight of water,
39 parts by weight of an isomeric mixture of 80% by weight of 2,4- and 20% by weight of 2,6-toluylene diisocyanate

to form an elastic foam which in the combustion test according to ASTM D—1692 is self extinguishing after burning for 13 to 20 mm.

A reaction product of 100 parts by weight of B and 3.5 parts by weight of methyl p-toluenesulphonate may also be reacted to form a self-extinguishing foam without being first mixed with A.

EXAMPLE 20

By reacting 100 parts by weight of D with 4 parts by weight of propanesultone, about 70% of the tertiary amino groups contained in D are quaternised. This product is reacted with 39 parts by weight of an isomeric mixture of 80% by weight of 2,4- and 20% by weight of 2,6-diisocyanatotoluene to form a prepolymer having an NCO content of about 10%. When 139 parts by weight of this prepolymer are stirred together with 1.5 parts by weight of permethylated diethylene triamine, 1.0 parts by weight of an organosiloxane-alkylene oxide block polymer and 2.9 parts by weight of water, an elastic foam is obtained which is self-extinguishing according to the ASTM test D—1692.

EXAMPLE 21

A mixture of 80 parts by weight of A,
20 parts by weight of B,
4 parts by weight of propanesultone,
0.5 parts by weight of an organosiloxane-alkylene oxide block polymer,
0.3 parts by weight of tin(II)-ethyl hexoate,
3 parts by weight of water, and
39 parts by weight of an isomeric mixture of 80% by weight of 2,4- and 20% by weight of 2,6-toluylene diisocyanate

is reacted and is expanded for about 60 seconds, to form an elastic polyurethane foam which burns for 15 to 25 mm in the ASTM D—1692 and is thus self extinguishing. In this list of components, the four parts by weight of propanesultone may be replaced by 4 parts by weight of methyl-p-toluenesulphonate, a self extinguishing foam being again obtained. The 20 parts by weight of component B may also be replaced by 20 parts by weight of component C (described below), in which case a foam which is self extinguishing after burning for 30 to 40 mm is obtained after an expansion time of 70 seconds.

EXAMPLE 22

100 Parts by weight of B are quaternised with 4.8 parts by weight of dimethylsulphate, the viscosity rising to 1990 cP_{25} within an hour.

63 parts by weight of this product are reacted with
37 parts by weight of A,
0.5 parts by weight of an organosiloxane-alkylene oxide block polymer,
0.3 parts by weight of diazadicyclooctane,
3 parts by weight of water and
39 parts by weight of an isomeric mixture of 80% by weight of 2,4- and 20% by weight of 2,6-diisocyanatotoluene,

the reaction mixture expanding for about 75 seconds to form an elastic foam which according to the ASTM test D—1692 is self extinguishing, burning for 30 to 40 mm.

EXAMPLE 23

100 Parts by weight of component B are reacted with 5.5% of propanesultone, the viscosity rising considerably without significant lowering of the OH number.

110 parts by weight of D quaternised with propanesultone are reacted with
90 parts by weight of A,
2 parts by weight of an organosiloxane-alkylene oxide block polymer,
0.2 parts by weight of tin(II)-ethyl hexoate,
2.6 parts by weight of permethylated diethylene triamine,
6 parts by weight of water and
78 parts by weight of the isomeric mixture of 80 parts by weight of 2,4- and 20 parts by weight of 2,6-diisocyanatotoluene,

the mixture expanding for 70 seconds to form an elastic foam which is self extinguishing in the combustion test according to ASTM D—1692.

EXAMPLE 24

100 Parts by weight of component D are reacted with 8.4% of methyl p-toluenesulphonate, the viscosity rising considerably without significant lowering of the OH number.

48 parts by weight of D quaternised with methyl p-toluene sulphonate and reacted with
52 parts by weight of A
1 part by weight of an organosiloxane-alkylene oxide block polymer,
0.15 parts by weight of tin(II)-ethyl hexoate,
0.8 parts by weight of permethylated diethylene triamine
3 parts by weight of water, and 41 parts by weight of the isomeric mixture of 80 parts by weight of 2,4- and 20 parts by weight of 2,6-diisocyanatotoluene, the components expanding for 50 seconds to form

an elastic foam which is self extinguishing in the combustion test according to ASTM D—1692.

EXAMPLE 25

200 parts by weight of B are reacted with
8 parts by weight of propanesultone,
1 parts by weight of an organosiloxane-alkylene oxide block polymer,
1.1 parts by weight of tin(II)-ethyl hexoate,
6 parts by weight of water, and
80 parts by weight of an isomeric mixture of 80% by weight of 2,4- and 20% by weight of 2,6-diisocyanato-toluene, the mixture expanding for about 40 seconds to form a polyurethane foam which according

to the ASTM test D 1692 is self extinguishing after burning for 30 to 35 mm. Instead of 8 parts by weight of propane sultone, 8 parts by weight of methyl p-toluene sulphonate may be used, a self-extinguishing foam being again obtained.

Foils 3 mm in thickness are cut from this foam and backed with nettle cloth in a conventional commercial flame backing plant. The plant operates at a rate of 10 m/minute, the gas pressure is 0.7 excess atmosphere and the gas flow is 30%. The resulting laminate is assessed for loss in thickness (combustion) in the course of the backing operation and for adhesion between foam and textile. The adhesion is examined both manually and mechanically. In the former case, the laminate is pulled apart by hand and the adhesion is characterised by marks varying from good to defective; in the latter case, a laminate strip 3 cm width is separated in a commercial tension tester in which the form is secured to one support and the textile to the other. The force (measured in kg.wt/cm^2) required for separating the laminate is determined.

	combustion mm	Adhesion of laminate	
		manual test	mechanical test
conventional polyether foam (3 mm thick)	1.0	defective	less than 0.2
Polyurethane foam produced according to the invention (3 mm thick)	1.0	good-satisfactory	0.5

Foils 3 mm in thickness are cut from the foam produced according to the invention in Example 25 and welded in a commercial high frequency welding apparatus (pressure 100 kg/cm^2, power 2 KW) to a PVC foil 0.2 mm thick. The nature and adhesion of the welding seam is assessed in relation to the welding time.

	Welding time in seconds	Current uptake (A)	Welding seam	Adhesion
conventional polyether foam	2	0.5	cloudy	moderate
	1.6	0.5	cloudy	moderate
	1.2	0.5	cloudy	moderate
	1.0	0.5	cloudy	moderate
	0.8	0.5	cloudy	moderate
polyether foam produced according to the invention	2	0.55	clear	very good
	1.6	0.55	clear	very good
	1.2	0.55	clear	very good
	1.0	0.55	clear	very good
	0.8	0.55	clear	very good

Polyethers A—D used in Examples 16 to 25 are characterised as follows:

A Branched polypropylene glycol polyether based on trimethylolpropane and propanediol-(1,2) in the ratio of 1:1 (OH number 56).

B Branched polypropylene glycol polyether (OH number 51) prepared by polypropoxylating 2-aminoethylpiperazine.

C Linear polypropylene glycol polyether having an OH number of 55, prepared by polypropoxylating piperazine.

D Linear polypropylene glycol polyether having an OH number of 57, prepared by polypropylating methylamine.

EXAMPLE 26

A. *Comparison tests*

The following components are mixed in the mixing chamber of a foaming machine which has a discharge rate of 19.2 kg. of polyether per minute;

100.0 parts by weight of a partly branched polypropylene glycol ether of OH number 46 which has been modified with terminal ethylene oxide groups,
6.5 parts by weight of water,
2.0 parts by weight of an organosiloxane-alkylene oxide block polymer,
0.2 parts by weight of 1,4-diaza-bicyclo-(2,2,2)octane,
0.25 parts by weight of tin(II)-ethyl hexoate and
79.0 parts by weight of toluylene diisocyanate (80% by weight of 2,4- and 20% by weight of 2,6-isomer).

The mixture is applied to the conveyor band of the foaming machine and foam formation sets in after a few seconds and is complete after further 50 seconds. A block of foam prepared according to the above recipe, measuring 2.50 m in length, 1 m in width and 55 cm in height starts to emit smoke after one hour and spontaneously ignites 1.5 hours after it has been produced.

B. *Foam according to the process of the invention*

The following components are reacted under the conditions mentioned above:

100.0 parts by weight of a partly branched polypropylene glycol ether of OH number 46 modified with terminal ethylene oxide groups,
6.5 parts by weight of water,
2.0 parts by weight of an organosiloxane-alkylene oxide block polymer,
0.2 parts by weight 1,4-diaza-bicyclo-(2,2,2)octane,
0.5 parts by weight of tin(II)-ethyl hexoate,
3.0 parts by weight of propane sultone, and
79.0 parts by weight of toluylene diisocyanate (80% by weight of 2,4- and 20% by weight of 2,6-isomer).

A block of foam of the same size produced under the conditions mentioned above does not ignite spontaneously.

EXAMPLE 27

The following components are mixed in the mixing chamber of a foaming machine, and the mixture is poured into moulds:

80.0 parts by weight of a slightly branched polypropylene glycol ether of molecular weight of 2500 and OH number 56,
20.0 parts by weight of a product of addition of propylene oxide to methylamine (OH number 57),
3.0 parts by weight of water,
0.37 parts by weight of permethylated diethylene triamine,
1.0 part by weight of an organosiloxane-alkylene oxide block polymer,
0.37 parts by weight of tin(II)-ethyl hexoate,
1.0 part by weight of trichloroethylphosphate,
4.0 parts by weight of propanesultone, and
41.0 parts by weight of toluylene diisocyanate (80% by weight of 2,4- and 20% by weight of 2,6-isomer) (identification number 105).

After an initial period of 4 seconds, the mixture becomes cloudy and after a further 62 seconds the expansion reaction terminates. The foam has the following physical properties:

Weight per unit volume:	34 kg/m^3
Tensile strength:	1.4 kg wt/cm^2
Elongation at break:	315%
Resistance to compression (40%)	31 p/cm^2.

When tested for flame resistance by the ASTM D—1692 test, the foam is found to have a combustion length of 22 mm.

EXAMPLE 28

The following components are mixed:

a) 86.5 parts by weight of a branched polyether, obtained by alkoxylation of trimethylol propane and 1,2 propane diol using a mixture of propylene oxide and ethylene oxide as epoxide (OH number 50; molecular weight about 3400)

b) 10.0 parts by weight of a polyether with an OH number 112 and a molecular weight of 1000

c) 3.5 parts by weight of N,N' - dimethyl-N,N' - bis - (2 - hydroxy - propyl)-ethylene diamine
d) 0.15 parts by weight of tin(II)-chloride
e) 1.0 part by weight of an organosiloxane alkylene oxide block polymer
f) 3.0 parts by weight of water
g) 43.5 parts by weight of toluylene diisocyanate (isomeric mixture of 80% 2,4- and 20% 2,6-toluylene diisocyanate)
h) 4.0 parts by weight of trichloroethyl phosphate
i) 2.0 parts by weight of propanesultone

The production of the foam can be effected be as follows:

1) Production of a mixture from a), b), and c)
2) Production of a further mixture from g), h) and i).

These two premixtures are separately brought into a mixing apparatus by pumps adding components f), e), and d), separately at the same time.

The premixtures as described above can be reacted with the remaining components either immediately or after any desired period to yield the same results.

The foam so obtained shows the following physical properties:

Weight per unit volume	33 kg/m^3
Tensile strength	1,4 kp/cm^2
Elongation at break	275%
Deflection hardness at 40% deflection	37 p/cm^2

The foam is slow burning. The combustion length amounts to 27—30 mm (ASTM D 1692).

Example 29

The following components A and B are mixed:

A 70 parts by weight of a branched polypropylene glycol ether based on trimethylpropane (OH number 56),
30 parts by weight of a linear polyether which contains tertiary amino groups and which is based on methylamine and propylene oxide (OH number = 57),
0.6 parts by weight of tin(II)-ethyl hexoate,
0.5 parts by weight of an organosiloxane-alkylene oxide block polymer,
3.0 parts by weight of water,

B 30.5 parts by weight of an isomeric mixture of 80 per cent by weight of 2,4- and 20% by weight of 2,6-diisocyanatotoluene,
7.5 parts by weight of hexamethylene-diisocyanate-(1,6),
40 parts by weight of propanesultone.

From the mixture of A and B one obtains, after an expansion time of 75 seconds, an elastic foam which according to the ASTM test D—1692 is self extinguishing and has a combustible portion of 40 to 45 mm.

Example 30

The following components are mixed:

A 98 parts by weight of a partly branched polypropylene glycol ether based on trimethylolpropane and propane-diol-(1,2) (OH number 56)
2 parts by weight of N,N' - dimethyl-N,N' - bis(2 - hydroxypropyl)-ethylene diamine,
0.5 parts by weight of tin(II)-ethyl hexoate
0.5 parts by weight of an organo-siloxane-alkylene oxide block polymer
3.0 parts by weight of water

B 30.5 parts by weight of an isomeric mixture of 80% by weight of 2,4- and 20% by weight of 2,6-diisocyanato-toluene
10.8 parts by weight of diphenylmethane-4,4'-diisocyanate
4.0 parts by weight of propane sultone.

The mixture of A and B immediately foams, and after about 90 seconds it yields an elastic foam with slightly closed pores, which according to the ASTM test F 1692 has a combustible portion of 20 to 25 mm and is self extinguishing.

Example 31

The following components are mixed:

A 98 parts by weight of a partly branched polypropylene glycol ether based on trimethylol propane and propane-diol-(1,2) (OH number = 56)
2 parts by weight of N,N' - dimethyl-N,N' - bis(2 - hydroxypropyl)-ethylene diamine
0.6 parts by weight of tin(II)-ethyl hexoate
0.5 parts by weight of an organo-siloxane-alkylene oxide block polymer
3.0 parts by weight of water

B 30.5 parts by weight of an isomeric mixture of 80% by weight of 2,4- and 20% by weight of 2,6-diisocyanato-toluene
10.8 parts by weight of a polyisocyanate according to German Patent Specification 1,092,007
4.0 parts by weight of propane sultone.

The foam obtained from the mixture of A and B is self extinguishing, having a combustible portion of 25 to 30 mm.

EXAMPLE 32

The following components A and B are mixed:

A— 100 parts by weight of a partially branched polypropylene ether, obtained from trimethylol propane and propane diol-1,2 (OH number 56; molecular weight about 2500)
1.0 part by weight of an organosiloxane alkylene oxide block polymer
0.5 parts by weight of tin-(II)-ethyl hexoate
3.0 parts by weight of water

B— 40.5 parts by weight of toluylene diisocyanate (isomer mixture of 80% 2,4- and 20% 2,6-toluylene diisocyanate)
3.0 parts by weight of propanesultone

The mixture of the above components starts to foam at once and yields an elastic foam after 100 seconds. According to ASTM test D—1692 the foam so obtained is self-extinguishing and produces a combustion portion of 40—50 mm.

EXAMPLE 33

The following components A and B are mixed:

A— 100 parts by weight of a partially branched polypropylene ether, obtained from trimethylol propane and water (OH number 56; molecular weight about 2500)
1.5 parts by weight of N,N'-dimethyl ethylene diamine
0.2 parts by weight of tin-(II)-ethyl hexoate
1.0 part by weight of an organosiloxane alkylene oxide block polymer
3.0 parts by weight of water

B— 42 parts by weight of an isomeric mixture containing 80% 2,4- and 20% 2,6-diisocyanato toluylene
3.0 parts by weight of propane sultone

A self-extinguishing foam is obtained. The burning part amounts to 30 to 35 mm (ASTM) D—1692).

EXAMPLE 34

The following components A and B are mixed:

A— 100 parts by weight of the polyether of example 33
1.0 part by weight of urea
0.3 parts by weight of tin-(II)-ethyl hexoate
1.0 part by weight of an organosiloxane - alkylene oxide block polymer
3.0 parts by weight of water

B— 32.6 parts by weight of the isomeric mixture obtained from 80% 2,4- and 20% 2,6-diisocyanatotoluylene.
10.9 parts by weight of the isomeric mixture obtained from 65% 2,4- and 35% 2,6-diisocyanatotoluylene
3.0 parts by weight of propanesultone

After a rising time of 70 seconds a soft elastic foam is obtained which is self-extinguishing. The burning part amounts to about 70 mm (ASTM D 1692).

If the following alterations are made:

A) 0.2 parts by weight of tin(II)-ethyl hexoate
B) 43.5 parts by weight of an isomeric mixture obtained from 80% 2,4- and 20% 2,6-diisocyanatotoluylene
2.0 parts by weight of propane sultone

and in addition

4.0 parts by weight of tris-(2-chloroethyl)-phosphate,

then a self-extinguishing foam is obtained after about 100 seconds, the burning part of which amounts to 30 to 40 mm.

WHAT WE CLAIM IS:—

1. A process for the production of polyurethane or polyurea foams in which polyethers which contain hydroxyl and/or primary or secondary amino groups, polyisocyanates, blowing agents and foaming catalysts are reacted in the presence of one or more cyclic or open chain esters of acids of hexavalent sulphur, which esters contain no reactive hydrogen atoms.

2. A process as claimed in claim 1 in which water is a blowing agent.

3. A process as claimed in claim 1 or claim 2 in which the polyether also contains tertiary amino groups.

4. A process as claimed in claims 1 or claim 2 in which a tertiary amine is used as foaming catalyst.

5. A process as claimed in any of claims 1 to 4 in which the nitrogen-containing polyether is wholly or partially quaternised by the ester of the acid of hexavalent sulphur and in which this quaternised polyether is subsequently foamed with polyisocyanates, blowing agents and foaming catalysts by the single or multistage process.

6. A process as claimed in any of claims 1, 2, 4, and 5 in which the polyether which contains no nitrogen is produced by polymerisation of alkylene oxides.

7. A process as claimed in any of claims 1 to 5 in which the polyether is produced by condensation of polyamines with alkylene oxides.

8. A process as claimed in any of claims 1 to 7 in which diisocyanates are used.

9. A process as claimed in any of claims 1 to 8 in which the esters of the acids of hexavalent sulphur are the corresponding monoesters.

10. A process as claimed in any of claims 1 to 8 in which the ester of the acid of hexavalent sulphur is an γ alkyl sultone.

11. A process as claimed in any of claims 1 to 8 in which the esters of the acids of hexavalent sulphur are C_1–C_3 alkyl substituted methyl benzene sulphonates.

12. A process as claimed in any of claims 1 to 11 in which 1 to 15 parts, by weight, of the esters of acids of hexavalent sulphur are used per 100 parts of polyether.

13. A process as claimed in claim 12 in which 2 to 5 parts by weight of the esters of acids of hexavalent sulphur are used per 100 parts of polyether.

14. A process as claimed in claim 1 for the production of polyurethane or polyurea foam plastics substantially as herein described with reference to any of the examples.

15. Polyurethane or polyurea foam plastics when prepared by a process as claimed in any of claims 1 to 14.

ELKINGTON & FIFE,
Chartered Patent Agents,
High Holborn House,
52/54 High Holborn, London, W.C.1.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1970.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.